

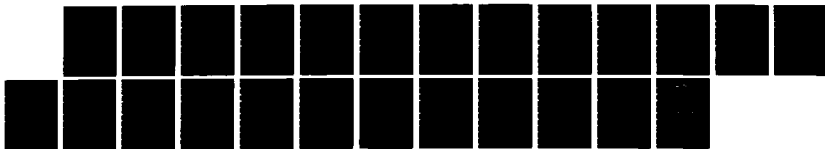
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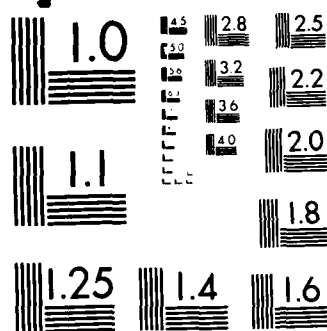
DEVELOPMENT OF PRACTICAL MO TECHNIQUES FOR THE  
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p>A "third generation" semiempirical SCF MO treatment (AM1) has been developed in which the weaknesses of MNDO, in particular failure to reproduce hydrogen bonds, have been overcome. MNDO has been parametrized for Zn, Hg, Ge, Sn, Pb, Br, and I and reparametrized for Si and S. A version of MNDO with d AOs has been parametrized for chromium. Our computer programs have been improved and collected into a single package (MOPAC) which allows calculations of a wide variety of molecular properties, and additional graphics packages developed. Calculations have been carried out for a wide range of chemical reactions and properties. The more important conclusions follow.</p> <p>(1) Extensive calculations for pericyclic reactions has led to a new general rule, that multibond processes are not normally synchronous. The Diels-Alder reactions in particular have been shown to involve unsymmetrical transition states.</p> <p>(over)</p>															
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19. (2) Studies of anionic nucleophilic substitution have shown that the barriers in solution can be due entirely to desolvation of the anion, a result of major theoretical significance.
- (3) Deriving from (2), a new explanation of the rates and specificities of enzyme reactions.
- (4) Refutation of FO Theory as an effective general treatment of chemical reactions.
- (5) A new interpretation of  $\sigma$  interactions in molecules (sigmaconjugation).
- (6) Evidence that tunnelling can play a more general role in chemistry than previously thought. ;

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## FINAL SCIENTIFIC REPORT

NOVEMBER 1, 1982 TO SEPTEMBER 30, 1985

Contract F49620-83-C-0024

Development of Practical MO Techniques for the Prediction  
of the Properties and Behaviour of Materials

Michael J. S. Dewar, The University of Texas, Austin, Texas 78712

Major progress has been made in a wide variety of areas through research supported by this Grant. The following is a brief summary with references to the papers (see List of Publications) giving the full results. General accounts have been published concerning the development of our procedures[13] and the relative merits of different quantum mechanical molecular models[40].

## New Procedures

A. AM1. After several years of intensive effort we have finally been able to develop an improved successor[43] to MNDO which avoids its major defects. In particular, it reproduces hydrogen bonds, gives satisfactory results for crowded molecules (e.g. neopentane), and leads to activation energies in better agreement with experiment (those from MNDO tended to be systematically too large). It also reproduces the properties of microcyclic compounds, in particular those with four-membered rings, much more effectively than MNDO. Even the heat of formation of cubane is well reproduced. Parameters have been finalized for C, H, O, and N. Parameters, which we think are final, are also available for the halogens (F, Cl, Br,



C. Extension of MNDO to Additional Elements. MNDO has been parametrized for germanium, tin[30], lead[49], zinc, and mercury[46], and reparametrized for silicon[56] and sulfur[50]. Extensive tests have shown the new parameters to represent a major improvement, especially for silicon. The sulfur parameters refer to an  $sp^3$  basis set and are therefore limited to  $S^{II}$ . A version of MNDO including d AOs (MNDOD) has been developed and attempts made to parametrize it for sulfur. To our surprise, inclusion of d AOs led only to a slight improvement in the results for  $S^{IV}$  and  $S^{VI}$ . We now believe the problem is primarily due not to the neglect of d AOs in MNDO but rather to the neglect of the changes in orbital size with effective atomic charge. The formal charges on sulfur in compounds of  $S^{IV}$  or  $S^{VI}$  its higher valence state are very large ( $\sim +3e$ ) and no allowance is made in MNDO for changes in the parameters due to the resulting orbital contractions. A version of MNDOD in which the parameters for the d AOs were made functions of the charge on sulfur led to quite reasonable results. However, the changes led to loss of the first order invariance of the bond order matrix to charges on geometry that characterize Hartree-Fock wave functions and which simplifies calculation of derivatives of the energy needed for geometry optimizations. As a result, calculations using this procedure require many times more computing time than MNDO. The basic idea, that orbital contraction is the key, has, however, led us to an alternative approach, not involving d AOs, which look promising. In the meantime, MNDOD has been parametrized for chromium, our first transition metal, and calculations for a wide variety of organochromium compounds and these reactions have given very encouraging results. Very extensive exploratory work was needed to effect this breakthrough. We hope that extension to other iron group metals, and then to

transition metals, in general, will now proceed with fewer problems.

#### New Techniques and Computer programs.

A. Sparkles. A useful addition to MNDO is an option for introducing an arbitrary number of disembodied point charges ("sparkles"), not associated with orbitals, which can be used to generate electrostatic fields, e.g. those due to ions or dipoles in the vicinity of the system being studied. One specific application has been in a new procedure[32] for calculating molecular polarizabilities, by finding the change in the electric dipole moment of a molecule when placed in a uniform electric field. Such a field can be generated by an appropriate array of sparkles. A simple extension allows hyperpolarizabilities to be calculated.

B. Location of Transition States. A new procedure has been developed for locating transition states of reactions, the only information needed being the geometries of the reactant and product[21]. While this does not always work, it usually does, and when it does it does so very efficiently.

C. Polymers. A program has been developed for studying one-, two-, and three-dimensional polymers, using MNDO in the tight binding approximation. A similar but less efficient program, for linear polymers only, was developed some years ago and shown to give good estimates of the geometry, vibration frequencies, and electronic band structure of polyethylene. The new program has given good results for a number of other polymers as well as polyethylene (where it reproduced the earlier



calculations) as well as for the difference in energy between diamond and graphite.

D. DRAW. This is a general purpose graphics program that allows molecules to be displayed in various representations (stride, ORTEP, etc.), rotated in any direction, and manipulated by changes in the geometrical parameters or addition or loss of atoms or groups of atoms. A version for TEKTRONIX terminals has been deposited with QCPE.

E. DENSITY. This program provides contour maps of electron density in arbitrary sections of molecules, either the total electron density or that in a particular orbital. The results have proved very helpful in interpreting electronic structures.

F. MODEL. This allows a molecule to be entered in the form of a structural formula on a graphics terminal display. An MM2 calculation then provides an initial three-dimensional geometry as input for MOPAC (see below). For cyclic systems, where starting geometries are often difficult to define, the saving in time and effort can be very great.

G. MOPAC. The MINDO/3 and MNDO computer programs have been rewritten and collated together in a single package (MOPAC) which is far simpler to use than the earlier versions and also allows procedures to be selected by the use of key words. MOPAC includes options for RHF, UHF, "half-electron", and CI calculations, with geometry optimization by the Davidon-Fletcher-Powell procedure; for the calculation of molecular vibration frequencies, derived thermodynamic quantities (entropy and specific heat), and kinetic isotope effects; and for the locating of transition states, either by the reaction coordinate method or by the new

procedure indicated above. MOPAC is now available from QCPE.

### Applications

Calculations have been carried out for a wide variety of chemical problems. These are discussed below, in a somewhat disordered manner since the topics treated are so varied.

A. Sigmaconjugation. The interpretation of bond localization in current textbooks rests on the assumption that the interactions between AOs of a given atom vanish. While this is true for pure s, p, etc., AOs, it is not true for hybrid AOs. Indeed, the resonance integral between two sp<sup>3</sup> AOs of a carbon atom amounts to ca 2.5 eV, more than double the  $\pi$  resonance integral between two adjacent 2p AOs in benzene! A detailed analysis[19] of the consequences of such sigmaconjugative interactions accounts for the apparent localization of bonds and also explains a number of hitherto puzzling anomalies, e.g. the remarkable stability of cyclopropane, the pyramidal structure of t-butyl radical, the bent structure of triplet carbene, and the unusual geometries of digermene, distannene, and diplumbene.

B. Inadequacy of Frontier Orbital Theory. A detailed study[63] of frontier orbital (FO) theory shows it to lack a proper theoretical basis, explains why it nevertheless often works well, and predicts failure in several specific situations. Calculations have shown that it does indeed fail in a number of such connections, often disastrously. Since PMO theory provides a better and more complete account of organic chemistry than does FO theory and since it also has a sound theoretical basis, the continuing

popularity of FO theory seems somewhat of an anachronism.

C. Reactivity of Silyl Halides. Detailed MNDO studies of the  $S_N2$  reaction, carried out earlier but only recently reported[22], agree with *ab initio* studies and experiment in predicting the trigonal bipyramidal intermediate to be a saddle point on the potential energy (PE) surface, i.e. the transition state (TS). While this conclusion has been accepted for many years, it is in fact surprising, given that simple MO theory predicts such a structure to be a *minimum* on the PE surface and given that many stable molecules are known where three collinear atoms are linked by a three-center four-electron bond similar to that in a  $S_N2$  TS. An obvious way to resolve this dilemma would be to suppose that the difference is steric in origin, a carbon atom being too small to form covalent bonds to five adjacent atoms. If so, the  $S_N2$  "TS" for substitution at a larger atom might be a minimum. MNDO calculations[9] indeed indicate this to be the case for nucleophilic substitution on silicon. The fact that silyl halides are more reactive than alkyl halides is therefore due not to d AO participation in the former, as confidently stated in all current textbooks, but rather to steric deactivation of carbon. The small size of the carbon atom is the factor that makes organic molecules so stable and life consequently possible.

D. Solvent Effects and Enzyme Reactions. MNDO calculations[34] for the reactions of a number of anionic nucleophiles with carboxylic acid derivatives predict them to take place without any activation whatsoever in the gas phase. If so, the barriers in solution must be due entirely to the energy needed to strip solvent from the anion so that the neutral carboxylic acid derivative can approach. This possibility has never been

seriously considered in the past because it seemed unreasonable that desolvation could lead to such large barriers and because the consequences for theoretical organic chemistry seemed so disturbing. Indeed, a preliminary communication reporting our results was rejected twice by JACS on the basis of reports by incredulous referees ("publication of this paper would do Professor Dewar's reputation no good!") so we finally published it in *Chem. Commun.*[34]). Unfortunately for our critics, a paper reporting very detailed ab initio calculations of solvent effects by computer simulation has recently appeared in the *J. Am. Chem. Soc.*, in complete agreement with our conclusions. The latter are obviously of major theoretical importance, not only in connection with solvent effects but for organic chemistry in general. In particular, they lead to a complete reassessment of the phenomena covered by the hard-soft-acid-base (HSAB) theory[34]. As we have also pointed out, they also lead to a novel and convincing explanation of the extraordinarily high rates and specificity of enzyme reactions[39]. Adsorption of the proper substrate of an enzyme in its active site is possible only if all inessential water is extruded from between them so any subsequent reaction takes place in the absence of solvent, i.e. as it would in the gas phase. *Solvactivated* reactions, i.e. ones where the barriers in solution are due solely to desolvation of ions, should then take place without activation under enzymatic conditions. This accounts immediately for their high rates and also for their specificity, because if an otherwise suitable substrate does not completely fill the active site, water will remain behind in it and will refind the reaction as it does in solution (*solvactivation barrier*). These ideas have been supported by model calculations for the individual steps in the hydrolysis of peptides by chymotrypsin[39].

E. Pericyclic Reactions. Calculations have been carried out for a wide range of reverse chelotropic reactions involving the loss of CO and N<sub>2</sub> from unsaturated rings[14,15]. The reactions were found to take place very unsymmetrically, one bond breaking completely, or almost completely, before the other, in agreement with earlier studies of the Diels-Alder reaction and with AM1 calculations[64] for the reactions of butadiene with ethylene, acrylonitrile, maleonitrile, fumaronitrile, and 1,1-dicyanoethylene.

Studies of the Claisen rearrangement indicated it to have a mechanism analogous to that found earlier for the Cope rearrangement, the reaction proceeding in effect by formation of the new bond before breaking of the old one[33].

These results, together with those from our earlier studies, led to the formulation[18] of a new rule for reactions which states that processes involving the synchronous formation and/or breaking of two or more bonds are disfavoured. The existence of this rule had been inferred some years ago, partly on the basis of our early studies and partly for consideration of a simple Evans-Polanyi-type treatment. Exceptions occur only in certain specific cases where special factors can be seen to favour synchronicity. Multibond reactions, i.e. ones involving the formation and/or breaking of more than one bond, otherwise invariably take place in steps or stages, each of one-bond type.

F. The C<sub>4</sub>H<sub>7</sub><sup>+</sup> potential surface. A detailed MINDO/3 study[28] of the C<sub>4</sub>H<sub>7</sub><sup>+</sup> potential surface has clarified the extensive experimental evidence concerning it. The most stable isomer is not as commonly supposed a

classical cyclobutyl cation but rather a protonated bicyclobutane, with a definite, though long, transannular CC bond and a "pentacovalent" bridgehead carbon. This explains why the ion is so much more stable than would be expected if it were the classical cyclobutyl cation. The other isomer, commonly formulated as the cyclopropylmethyl cation, also has a nonclassical structure, being in fact the  $\pi$  complex derived from ethylene and vinyl cation. It is stabilized by back coordination of vinyl  $\pi$  electrons into the empty antibonding  $\pi$  MO of the ethylene. This isomer is a little higher in energy than the protonated cyclobutane and separated from it only by a low barrier. Ring opening involves crossing a high energy barrier and leads not to 3-butenyl cation but directly to 1-methylallyl cation. The formation of 3-butenyl derivatives by extended solvolysis of cyclopropylmethyl esters must therefore be attributed to nucleophilic attack by solvent on the  $\pi$  complex.

G. Biomimetic cyclizations. A detailed MINDO/3 study[20] of the cyclization of deca-5,9-dienyl cations indicated them to take place via intermediate  $\pi$  complexes. The stereospecificity of multiple cyclizations of this kind, e.g. in the synthesis and biosynthesis of steroids and triterpenes, is therefore due to the intermediates being  $\pi$  complexes, not to synchronous closure of the individual rings.

H. Benzene Dication. Studies of dications corresponding to benzene and its derivatives indicate them to exist in two alternative forms; one a pentagonal pyramid, the other a chair-type monocycle[29]. The relative stabilities of the two isomers depends on the substituents. This work accounts nicely for the available experimental evidence concerning species of this kind.

I. Benzyne. Calculations[12] for the three didehydrobenzenes (benzyne) account well for their observed properties and confirm earlier suggestions that the 1,3 and 1,4 isomers can exist in two stable isomeric forms, one a monocyclic biradical-like species and the other a bicyclohexatriene. The calculations support a suggestion, that the biradical form of the 1,4 isomer is an intermediate in the degenerate rearrangement of divinylacetylene. MNDO calculations were used to assign the photoelectron spectrum of benzyne[53].

J. Didehydrodiazines. MNDO calculations for all the possible didehydrodiazines (diazynes) account for the rather scanty experimental evidence concerning them and lead to numerous predictions concerning their stabilities and chemical behaviour[25].

K. Didehydrocyclooctatetraenes. MNDO calculations have been carried out for a number of  $C_8H_6$  species derived from cyclooctatetraene by loss of two hydrogen atoms and for their interconversions[54].

L. Pericyclynnes. MNDO calculations[26] for [3], [4], and [5]pericyclyne account well for their observed behaviour and lead to interesting predictions concerning [3]pericyclyne and its relationship to the isomeric triscyclopropabenzene.

M. Succinimidyl Radical. MNDO calculations[36] for ring opening of the succinimidyl radical support recent suggestions by Skell concerning the existence of the radical in both p and s forms; cf[6].

N. Chair Cyclooctatetraene. MNDO calculations[37] indicate that the chair isomer of cyclooctatetraene, with two trans double bonds, should be a reasonably stable species, implying that attempts to synthesize suitable derivatives could be profitable.

O. Organotin Chemistry. Extensive calculations have been carried out for a number of organotin compounds and their reactions[30,31,44,45,47,62]. The results have clarified experimental results in a number of areas, in particular the properties and reactions of organotin radical cations, of 2,4,6-trithia-1,3,5-tristannaadamantane, and of compounds of divalent tin. The tin atoms in distannene are predicted to be pyramidal, the tin atoms being linked by a sigmaconjugated double bond (see[19]).

P. Organolead chemistry. A number of problems in organolead chemistry are discussed in the paper[51] reporting MNDO parameters for lead.

Q. The Azulene-to-Naphthalene Rearrangement. The rearrangement of azulene to naphthalene is a remarkable reaction. Much work has been directed to elucidating its mechanism. MNDO calculations[57] indicate that neither of the mechanisms currently under consideration is correct and lead to a plausible alternative.

R. Cruciaromaticity. It was pointed out some years ago that the  $\pi$  MOs in phosphonitrilic compounds are not cyclic but rather consist of three-orbital allylic units that cross one another without interaction at each phosphorus atom, the latter using two different d AOs for its contributions to the two different allylic moieties. Similar cruciconjugation seems to occur in compounds such as the thiabenzene and



phosphabenzenes and in certain transition states, in particular those for hydroboration reactions. It has now been pointed out[58] that transition metal complexes of unsaturated chelating ligands can contain cyclic cruciconjugated rings, crossing at the central metal atom which uses different d AOs to  $\pi$  bond to the adjacent ligand atoms. Such rings can of course be aromatic, i.e. cruciaromatic. The structures of a number of such compounds are discussed in terms of their potential cruciaromaticity or cruciantiaromaticity.

S. Energies of Excited States. In order to provide basis information concerning the applicability of MNDO to photochemical reactions, calculations have been carried out for the lowest singlet and triplet excited states of a wide variety of unsaturated molecules[27]. While the errors are commonly much larger than for ground states, sometimes amounting to >30 kcal/mol., they seem to be mostly systematic. It therefore seems likely that the error will remain much the same over the sections of potential surfaces involved in photochemical processes.

#### Tunnelling.

While the role of tunnelling in degenerate reactions involving migrations of hydrogen atoms (e.g. ammonia inversion) has long been recognized and while tunnelling has also been shown to play a significant role in certain bimolecular hydrogen transfers, little attention has as a rule been given to its possible intervention in other cases. Interest in it has, however, been raised recently by Carpenter's arguments for the intervention of heavy atom tunnelling in the degenerate valence

tautomerization of cyclobutadiene. We have now studied[23] this reaction by a better procedure (method of periodic orbits) than that used by Carpenter and find the rate of tunnelling to be even larger than he had supposed. We have now carried out detailed studies of several other systems involving analogous degenerate rearrangements (cyclopropane and cyclobutane radical cations, cyclopropenyl radical and anion) and find tunnelling to play a major role in all of them[55].

The examples of tunnelling so far considered have nearly all involved tunnelling from vibrational ground states of molecules. While the possibility of tunnelling from vibrationally excited states has naturally been recognized, it has been largely ignored because of the lack of any satisfactory procedure for estimating its rate. We have now developed[55] a simple but effective procedure for estimating the rates of such vibrationally assisted tunnelling (VAT) approximately and have used it to find evidence for VAT in two well studied reactions.

(a) MNDO calculations[55] for the degenerate rearrangement of 1,3-pentadiene by 1,5 migration of hydrogen indicated it to take place largely by VAT in the temperature range used in the experimental study by Roth et al. This explains their otherwise surprising observation of an unprecedentedly large deuterium isotope effect in the rearrangement of deuteriated pentadiene and also the fact that the H/D rate ratio had a very large temperature coefficient.

(b) A detailed study of the degenerate rearrangements of cyclooctatetraene, by tub-to-tub inversion or by interchange of single and double CC bonds, indicated[55] the latter to take place by heavy atom VAT.

The fact that the rates of the two processes differ so little has been otherwise hard to explain because it should be equal to the difference in energy between the  $D_{4h}$  planar form of cyclooctatetraene, with alternating C=C and C-C bonds, and the symmetrical planar ( $D_{8h}$ ) structure with all bonds equal. Since cyclooctatetraene is antiaromatic, this difference is expected to be quite large, being equal to the antiaromatic energy of planar  $D_{8h}$  cyclooctatetraene.

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- [23] Tunnelling Dynamics of Cyclobutadiene (Michael J. S. Dewar, Kenneth M. Merz, Jr., and James J. P. Stewart) J.A.C.S., 106, 4040-4043.
- [24] Ground States of Molecules. 67. MNDO Calculations for Compounds Containing Iodine (Michael J. S. Dewar, Eamonn F. Healy, and James J. P. Stewart) J. of Compt. Chem., 5, 4, 358-362.
- [25] MNDO Studies of Didehydrodiazines (Michael J. S. Dewar and Daniel R. Kuhn) J.A.C.S., 106, 5256-5261.
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